Abstract

Recent years have seen a rapid expansion in the acquisition and use of information on diffusive transport in phases relevant to the solid Earth (crystals, melts and fluids). Although far from complete, the database on diffusion coefficients is now sufficiently large that broad constraints can be placed upon the length- and time scales of many natural transport phenomena in which diffusion plays a role. Conversely, observations of diffusion progress in specific natural samples can be used to extract time–temperature information for a variety of geologic and geochemical processes, ranging from sediment burial and crustal erosion to fluid-mediated reactions and biosignature retention.

Despite this undeniable progress, several major challenges remain that largely define the frontiers of research in solid-Earth diffusion. Perhaps foremost among these is the need to address and understand the multi-scale, multi-path aspects of diffusion in many systems—a complication that is not limited to polyphase materials (individual mineral grains can exhibit clear indications of multi-path behavior even when visible evidence of such paths is lacking). Many other diffusion frontiers are linked in one way or another to this multi-scale issue; they include: diffusion of molecular H$_2$O and the effect of H species on diffusion in minerals and rocks; diffusive fractionation of multiple isotopes of a single element; diffusion at the extreme conditions of the deep Earth; reconciliation of observations from natural samples and laboratory studies; and development of theoretical approaches to ‘predict’ diffusion behavior in regions inaccessible to observation.

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1. Introduction

This contribution is not intended as a comprehensive review of diffusion theory, a compendium of geologically relevant diffusion data, or a ‘how-to’ guide to diffusion measurements. Rather, it is a broad characterization of the state of understanding of diffusion in geological systems emphasizing both what we already know and what we need to know. It is a perspective that we hope will be of interest to the broader community of scientists concerned in some way and at some level with mass transport and atomic mobility in the Earth. In keeping with the spirit and intent of Frontiers articles, we are writing for non-specialists with the objective, first, of building a basic knowledge base. We then proceed to a discussion of the substance, goals and challenges of current research activities.

The phenomenon of diffusion is important in all of Earth’s systems (atmosphere, hydrosphere, cryosphere,
soils, sediments, and deep subsurface), but for practical reasons we restrict the scope of this paper to the solid Earth. In this realm, diffusion contributes to chemical transport and exchange at scales ranging from nanometers to kilometers. Even when diffusion by itself does not result in long-range mass transport, it may augment or control the effects of advective mass transfer. It could be said that at some finite length scale, diffusion becomes a rate limiting process in any dynamic system. The multiplicity of scales at which diffusion is important will be a recurring theme of this article.

The relevant length scales of the vast majority of geochemical applications of diffusion fall in between the two extremes noted above; these include: geo- and thermochronology; geospeedometry; reaction rates; solid-state grain growth and microstructure development; homogenization of mineral grains; coarsening of grains and pores; growth of bubbles from liquids; dissolution and growth of crystals; rheological properties of solids and magmatic liquids; magma mixing; and bulk diffusion through rock. We will touch on some but not all of these topics, emphasizing areas of current excitement in solid-Earth geochemistry where further research is especially needed.

2. Basic concepts

2.1. Definition and overview

In common scientific usage, the term “diffusion” refers to the translational motion of atoms or molecules dissolved in a phase. In general, the reference frame for gauging motion of the atoms of interest is the lattice (in the case of a crystal) or structure of the host phase. Diffusion theory is typically put forth in separate but complementary approaches: atomistics (deductions based upon consideration of the random motion of individual atoms) and phenomenology (the empirical equations governing diffusion in a continuum). These are described only in the most general terms here; for comprehensive, readable treatments with varying emphasis, the reader is referred to Shewmon [1], Manning [2], Cussler [3] and Glicksman [4].

2.2. Atomistic and molecular-scale considerations

Classical atomistic treatments of diffusion usually begin by considering a simple, rigid lattice characterized by atoms in a specific coordination with their neighbors. This framework is fairly realistic for some Earth materials (e.g., simple oxides), less so for complex silicates, and ill-suited in varying degrees for melts and fluids. Some of the basic concepts of the ‘lattice-bound atom’ approach are nevertheless readily transferred to structurally complex materials. The essential idea is that a constituent atom or ion oscillating in a fixed position has the potential to vacate this position and ‘relocate’ a short distance away. This displacement constitutes a diffusive ‘jump’, and amounts to a net migration of the atom. Several mechanisms allow or facilitate the diffusive jump (see Fig. 1).

The basic concept of a jump frequency is relevant to diffusion in all materials having a more-or-less rigid atomic structure, but it is not a suitable conceptualization for diffusion in gases and supercritical fluids, where much of the kinetic energy of individual molecules is contained in their continuous translational motion. In supercritical C–O–H fluids, for example, it may be more accurate to think in terms of solute molecules or ions migrating through an inviscid

Fig. 1. Schematic representation of selected diffusion mechanisms for crystalline solids. The vacancy and interstitial mechanisms are common and well documented; the others are largely hypothetical and have not been confirmed in minerals. See Manning [2] for a detailed treatment.
continuum. The ‘rigid lattice’ and ‘inviscid continuum’ ideas represent the end-member ways of thinking about diffusion in the full the range of (condensed) geologic media (see Text Box 1). Interestingly, silicate melts could be regarded as falling between the two end-member models, depending upon the composition (hence the degree of polymerization) of the melt and the identity of the diffusant.

Box 1

Diffusion in geological materials: rigid lattice or inviscid continuum?

Diffusion involves the random motions of individual atoms within the large collections of atoms we call phases. The inherent diversity of Earth materials – liquid, crystal, supercritical fluid – requires several atom-scale conceptualizations of diffusion. Which of these is most accurate in a given case depends mainly upon the dominant form of the kinetic energy of the constituent atoms or molecules: translational, vibrational, or both. Two conceptualizations of diffusion are illustrated below.

Rigid lattice. Atoms oscillate about a generally fixed position, occasionally jumping to a neighboring site. Here, long-range migration of an atom requires a sequence of discrete jumps whose frequency is given by \( \Gamma = v \exp(-E/kT) \), where \( v \) is the vibrational frequency of the atom on the site, \( E \) is the energy barrier that must be overcome during the jump, \( k \) is Boltzmann’s constant and \( T \) is temperature in Kelvins.

Example: Pb diffusion in zircon.

Inviscid continuum. The momentum of larger atoms or molecules (generally solute) carries them through a ‘sea’ of smaller molecules (solvent) that exert a viscous drag. Here the diffusivity is accurately ‘predicted’ by the Stokes–Einstein equation, \( D = kT/(6\pi\eta R_o) \), provided that the radius of the solute species is less than 5X that of the solvent species [155]; \( \eta \) is the fluid viscosity and \( R_o \) is the radius of the solute diffusant.

Example: diffusion of SiO_2 solute in supercritical aqueous fluid.
2.3. Phenomenology: the basic equations

2.3.1. Fick’s laws

Through random motions of its constituent atoms, an initially heterogeneous phase will eventually reach a state of homogeneity due to fluxes of atoms from regions of high concentration (strictly, chemical potential; see Section 2.3.2) to low concentration. In 1855 Adolph Fick formalized this observation by asserting (and later showing consistency with experiment) that

$$J_i = -D_i \frac{\partial c_i}{\partial x}$$

where $J_i$ is the flux of species $i$ through the medium of interest (units of $J_i$ are atoms per unit time passing through unit area $\perp x$), $\partial c_i/\partial x$ is the concentration gradient of $i$ in the $x$ direction, and $D_i$ is a constant that we now recognize as the diffusion coefficient or diffusivity (units = m$^2$/s) for species $i$ in the specific medium of interest. Eq. (1) is a 1-dimensional flux equation, so concentration gradients in directions other than $x$ are implicitly assumed to be zero. As expected, $J_i$ goes to zero as $\partial c_i/\partial x$ goes to zero, but it is important to realize that it is actually the net flux in the $x$ direction that goes to zero. This is Fick’s first law, also called the steady-state diffusion equation because $\partial c_i/\partial x$ and $J_i$ are not explicitly time-dependent. There are relatively few instances in geochemical systems where the steady state truly holds, but this does not diminish the conceptual and intuitive value of this equation.

Fick’s more general mass-conservation equation is (for one-dimensional diffusion with $D_i$ independent of $x$ and $c_i$)

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial x^2}$$

Box 2

Multi-dimensional diffusion

The non-steady state diffusion equation for three dimensions is

$$\frac{1}{D_i} \frac{\partial c_i}{\partial t} = \frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2}$$

but the most common approach to dealing with multi-dimensional diffusion is to approximate the geometry of the object or system of interest by a simple shape such as a cylinder or sphere in which diffusion is assumed to be radially symmetric. For these simple shapes, equations analogous to (2) express $c_i$ as a function only of radial position ($r$) and time:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial r} \left( r \frac{\partial c_i}{\partial r} \right)$$

for a cylinder

and

$$\frac{\partial c_i}{\partial t} = D_i \left( \frac{\partial^2 c_i}{\partial r^2} + \frac{2 \partial c_i}{\partial r} \right)$$

for a sphere

See chapters 5 and 6 of Crank [5] for analytical solutions to these equations for various boundary conditions. Note also that numerical (finite difference) solutions are readily implemented with these equations, so we have ready escape from the limitations of $D_i$ being independent of both $r$ and $t$, and from restrictive boundary conditions (e.g., constant surface concentration).

Fig. 2. Two illustrations of ‘uphill’ diffusion. A: Bulk-rock example in the form of uphill Nd diffusion near the contact of Archean-age tonalite and amphibolite rocks from Greenland. Dashed lines show inferred initial Nd rock concentrations before diffusive exchange. Diffusion appears to have been driven by a chemical potential gradient in Nd that did not correlate with concentration across the lithologic contact (E.F. Baxter and D.J. DePaolo, unpublished data). B: Uphill diffusion of Ca during chemical interdiffusion of CaO–Al$_2$O$_3$–SiO$_2$ melts at 1500 °C and 1 GPa for 1 h [8].
This equation describes the change in local concentration with time ($t$), and so is referred to as the nonsteady-state diffusion equation (and also as Fick’s second law). Solutions have been obtained for many different boundary conditions; a summary can be found in the classic reference work by Crank [5]. Many geo-logic applications involve chemical gradients in more than one direction, for which a multi-dimensional form of Eq. (2) is needed (see Text Box 2).

2.3.2. Complications

In Eqs. (1) and (2), $D_i$ for a given medium is implicitly constant. However, situations may arise in which $D_i= f(c_i)$ if $c_i$ varies substantially, as in a solid solution or melt. Dependence of $D_i$ upon $c_i$ may be inevitable due to changing thermodynamic influences of other components of the solution. Eq. (1) can be stated in words as “a gradient in concentration will lead to an observable flux”—but a more rigorous wording is required by chemical thermodynamics: “a gradient in chemical potential ($\mu_i$) will lead to an observable flux.” At low concentrations where Henry’s law applies (as for trace elements) diffusion within a single phase generally obeys the simple forms of Fick’s laws, because $\mu_i$ is proportional to $c_i$. However, when major components are involved, or when considering diffusion across a phase boundary, concentration gradients alone generally are not adequate to describe system behavior. For example, thermodynamic influences can actually lead to ‘uphill’ diffusion of a given component; that is, cases where the net flux of $i$ occurs with the chemical potential gradient, $\mu_i$ (as required) but against the concentration gradient in $i$. Geochemical examples may be surprisingly

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**Box 3**

‘Types’ of diffusion

Some practical definitions are useful when discussing diffusion in geological materials. These vary somewhat among authorities and disciplines, but there is general agreement on the essential characteristics.

**Self diffusion** refers to the migration of the constituent atoms of substance in the absence of chemical gradients (the ‘random-walk’ idea). Geochemists tend to use the term ‘isotopic diffusion’ for the same phenomenon, but in geological systems it is probably rare that isotopic heterogeneity with respect to a specific element would exist in the absence of gradients in concentration of that element. Isotopic tracers are generally needed to characterize self diffusion, so the term ‘tracer diffusion’ is often equated with self diffusion.

**Chemical diffusion** refers to diffusion in a chemical potential ($\mu$) gradient, for which conditions are widespread in natural systems. Approaches to the study of chemical diffusion range from the practical to the complex. In a binary system, diffusive mixing is generally described by an **interdiffusion coefficient** defined simply in terms of Fick’s first law:

$$\tilde{D}_i |_x = -J/(dc/dx)$$

$\tilde{D}$ generally varies with concentration (i.e., with distance across the interdiffusion zone), but this can be addressed using the Boltzmann–Matano approach (see Shewmon [1], pp. 34–37). Chemical diffusion in multicomponent systems becomes complicated because interdiffusing species experience ‘thermodynamic’ effects on top of their intrinsic mobilities (the concentration of one component may affect $\mu$ of another). For systems of more than 2 components it may be expedient to use an **effective binary diffusion coefficient** (EBDC; see [156,157]), but rigorous treatment of multicomponent diffusion involves determination of the diffusion coefficient matrix defined by Onsager’s [158] extended version of Fick’s first law:

$$J_i = \sum_{j=1}^{n-1} D_{ij} \left( \partial c_j / \partial x \right)$$

where $n$ is the number of components in the system ($n − 1$ of the diffusivities are independent). See the textbooks cited in Section 2.1 and [6,10,159–161] for more discussion.
common, and include interdiffusion of silicate melts (e.g., [6–8]), near-surface diffusion phenomena in minerals [9], and chemical diffusion across phase or lithologic boundaries ([10]; see Fig. 2). Use of appropriate boundary conditions taking into account the difference in the $\mu_i=f(c_i)$ relationship (i.e. the partition coefficient) is frequently sufficient in the modeling of diffusive exchange between phases.

The foregoing considerations necessitate a general classification scheme for ‘types’ of diffusion that might apply to atom migrations within a single phase such as an individual crystal or a volume of melt (Text Box 3). For the most part, these definitions address the nature of the gradients (if any) that diffusion tends to eliminate. They do not consider diffusion pathways—the subject of the next section—but is worth noting that a particular type of diffusion as described in Text Box 3 could take advantage of any pathway.

2.3.3. Diffusion pathways in geologic media

Classical treatments of diffusion typically recognize several distinct diffusion paths in polycrystalline materials: 1) volume (or lattice) diffusion refers to atomic migrations occurring within a single crystal; 2) grain-boundary diffusion involves migrations along two-dimensional regions between the mismatched lattices of individual grains; 3) defect diffusion describes migrations along extended intracrystalline defects such as dislocations; and 4) surface diffusion refers to migration along (parallel to) a crystal surface against a vacuum or a fluid medium. In geological systems, the relative importance of these ‘classical’ paths depends upon the phenomenon or process of interest. In isotopic studies of individual crystals, for example, intragrain diffusion is a primary concern, but may not be controlled entirely by lattice diffusion because extended defects can play a role (see below). Surface diffusion may enter into nanometer-scale phenomena such as migration to step edges during crystal growth from a fluid [11]. Diffusion along boundaries between mineral grains probably determines the overall effectiveness of bulk transport in rocks (Section 3.2), but there may be complexities not encountered in simple ceramics and metals. Rocks at depth in the Earth can be complicated by the presence of intergranular fluid, and even when a free fluid is lacking, the grain- and interphase boundaries may be laden with incompatible ions—including C–O–H species—which might impart diffusion qualities quite different from those of grain boundaries in relatively pure materials. When fluid is present, the long-range connectivity depends upon the mineral/fluid wetting characteristics, which are affected by the compositions of both phases [12]. If stable grain-scale connectivity is achieved, the fluid geometry is that of a grain-edge network—which does not wet the interfaces between grains (i.e., the grain boundaries) under conditions of chemical and mechanical equilibrium (but see [13]).

Earth materials are complicated still further by the fact that each individual mineral grain may be, in a sense, a microcosm of the host rock, with multiple pathways available for diffusion within the grain itself (Fig. 3). Generally speaking, lattice diffusion by site-to-site jumping of atoms will constitute the slowest intracrystal ‘path’, but the overall diffusive response of a mineral grain to a disequilibrium condition may depend upon the presence and number of fast paths, which could include 2-D features (e.g., sub-grains; exsolution boundaries), as well as 1-D edge and screw dislocations. These types of features logically constitute the fast diffusion paths in multi-path diffusion models and the domain boundaries in the multi-domain diffusion (MDD) model (Text Box 4). Diffusive fluxes normal to—but within a few nanometers of—a surface or grain boundary may influence the uptake of impurities during crystal growth [9]. In this case the
governing diffusivities may resemble values pertaining to grain boundaries.

2.4. Diffusion at depth in the Earth: general effects of \( T \) and \( P \)

2.4.1. Temperature dependence

From the discussion in Section 2.2, it follows that diffusion is a temperature-dependent phenomenon: no matter what atomistic model is envisioned to apply in any specific case, the increased kinetic energy associated with higher temperature means greater atom mobility. In the site-jumping model, the diffusivity is proportional to the jump frequency and so is expected to show, qualitatively, the same dependence upon temperature (Text Box 1). The temperature dependence of \( D \) predicted by the Stokes–Einstein relation (Text Box 1) is difficult to evaluate because the viscosity (\( \eta \)) of the solvent is itself temperature dependent. In most experimental characterizations of diffusion in geologic media, \( D \) varies with \( T^{-1} \) in log-linear fashion within the uncertainty of the measurements. In a very broad

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**Box 4**

“Multiple-path diffusion” jargon

The following terms have been used to describe individual systems characterized by spatially variable diffusion characteristics. All definitions incorporate the idea of discrete ‘slow’ and ‘fast’ diffusion pathways (domains) and the diffusion timescales associated with each. In all but the multi-domain diffusion case, the equilibrium partitioning of the diffusant between the slow and fast paths is a fundamental property of the system.

**Multi-domain diffusion**: frequently abbreviated MDD [47], this concept has been popularized mainly in thermochronologic applications of Ar diffusion in potassium feldspars. The MDD model describes intragrain diffusive loss controlled by multiple intragrain domain sizes (of dimension \( a_1, a_2, a_3\ldots \)) each with the same \( D \), and separated from each other by domain boundaries (fast paths) with infinite diffusivity. Net diffusive loss of Ar from a MDD mineral is controlled by \( a_i^2 / D \) of each domain population \( (i) \) and its volumetric fraction in the mineral.

**Multi-path diffusion**: connotes the presence of multiple intragrain pathways characterized by fundamentally different \( D \), and probably also different characteristic diffusion length scales \( (a) \). These intragrain pathways may include the lattice (slowest pathway), as well as “pipes” or planar features consisting of defects or nanopores (see Fig. 3) within and along which diffusion proceeds at a faster rate. Multi-path diffusion has also been referred to as “fast-path”, “short circuit”, or “pipe” diffusion [162]. Multi-path diffusion differs from the MDD concept only in that the diffusivities of the fast paths are not treated as infinite. Thus diffusive loss from such a mineral is governed by the combined effects of the fast path diffusivity and slow intragrain diffusion providing diffusant to (or accepting it from) the fast paths.

**Bulk diffusion**: connotes diffusion through a rock or other porous medium where the minerals and the intergranular region (ITM) that surrounds them have fundamentally different properties. It is often the case that the ITM can accommodate much faster diffusion, so the bulk diffusivity of that rock may be governed mainly by the properties and abundance of the ITM. For this to be true, however, the diffusant of interest must be sufficiently concentrated in the ITM, as discussed in Section 3.2. Bulk diffusion in its simplest conceptualization requires that the ITM and the solids maintain equilibrium with respect to the diffusant of interest.

**Double-diffusion**: essentially a more general term for bulk diffusion where the requirement of equilibrium between mineral grains and ITM is relaxed. Here, the net rate at which a diffusant is transported through a rock system is governed by the diffusion properties of both the ITM and the mineral grains. The ratio of the diffusive timescale for the ITM and the diffusive timescale for equilibration of the solids (called a diffusion-exchange parameter, \( D_e \)) is useful in characterizing net system behavior for the length scales of interest. (Note: Double-diffusion in the present context should not be confused with double-diffusive convection, which applies to magma chambers and involves diffusion of heat and matter; see [163])

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sense, then, the diffusivity of a given species \((i)\) in a particular medium conforms to the Arrhenius equation

\[
D_i = D_0, i \exp(-E_a / RT)
\]

where \(D_0\) and \(E_a\) are temperature-independent constants and \(R\) is the gas constant. In principle, the pre-exponential constant \(D_0\) contains attributes of the diffusion medium such as site type and lattice characteristics, but this has not proven useful in predicting diffusion behavior in complex crystals such as silicates, apart from empirical correlations. The activation energy for diffusion, \(E_a\), varies enormously, the extreme range being from \(\sim 40 \text{ kJ mol}^{-1}\) for CO\(_2\)–H\(_2\)O interdiffusion in supercritical fluid [14] to several hundred — e.g., \(\sim 700 \text{ kJ mol}^{-1}\) for diffusion of C in diamond [15] and \(\sim 800 \text{ kJ mol}^{-1}\) for diffusion of tetravalent cations in zircon [16]. Both the absolute value of \(D\) and its sensitivity to temperature correlate in a broad sense with parameters such as atom packing density (‘ionic porosity’), bond strength (as gauged, for example, by ionic charge), and lattice rigidity [17–19].

2.4.2. Pressure dependence

Theories addressing the effect of pressure on \(D\) are well developed for simple crystals and van der Waals liquids (see, e.g., [1,20]). In general, it has been shown that

\[
D_{T,P} = D_T \exp(-PV_a / RT)
\]

where \(D_{T,P}\) is the diffusivity at some temperature and pressure, \(D_T\) is the ‘zero-pressure’ diffusivity at the same temperature (given by Eq. (3)) and \(V_a\) is a constant characteristic of the diffusant and the medium, having the units of volume. The atomistic significance of \(V_a\) (called the activation volume) depends upon the operative diffusion mechanism [1], and it is not in fact always constant over large changes in \(P\) or \(T\). The interpretation of \(V_a\) in melts and glasses is uncertain, but there are examples in which its value approximates the volume of the diffusing entity [21,22] — which implies that the effects of pressure on diffusion will be most significant for large ions. For Mg\(^{2+}\) = Fe\(^{2+}\) interdiffusion in olivine [23], \(V_a\) exceeds the molar volume of the cations (~ 1.3 cm\(^3\) mol\(^{-1}\)), closely approaching that of O\(^{2-}\) (~ 5.5 cm\(^3\) mol\(^{-1}\)). Apparently negative values of \(V_a\) — i.e., \(D\) increasing with increased pressure — have been observed for diffusion in silicate melts (e.g., of Al; [24]), but this behavior is generally attributed to \(P\)-dependent aspects of the melt structure.

Despite the importance of pressure as a geologic variable, there exists comparatively little information on the effect of pressure (relative to temperature) on diffusion (see recent review by Béjina et al. [25]).

Based on the available evidence, it seems safe to generalize that pressure has a minor influence over the \(P\) range relevant to the Earth’s crust, where variations in \(D\) attributable to \(\Delta P\) would rarely be as high as a factor of
3. In the mantle, however, the pressure effect may rise to prominence, as suggested by recent studies (e.g., [26–28]). Because we see pressure effects as a frontier in diffusion research, this topic will be revisited later.

2.4.3. Diffusivities in Earth materials

A comprehensive summary of the vast literature reporting diffusion measurements on natural materials is precluded here (see Brady [29]; Béjina et al. [25]). A practical, broad-brush characterization is presented in Fig. 4, which illustrates the overall range of \( D \) values and their temperature dependence for both crystals and fluids. In order to convey the length scale over which diffusion could be effective in various geologic media, the figure shows characteristic diffusion distance, \( x \approx \sqrt{D t} \), as a function of \( D \) for time scales ranging from 1 to \( 10^9 \) yr.

3. Solid-Earth diffusion frontiers

3.1. Prologue

Several areas of diffusion research are particularly exciting in terms of both recent discoveries and foreseeable future developments. Due to space constraints, the following sections can convey only the flavor of current frontiers in diffusion rather than an exhaustive discussion. In some instances, we will focus upon specific findings; in other cases we will offer an integrative perspective that we hope will enable the reader to appreciate key phenomena, applications and challenges.

3.2. Diffusion in heterogeneous media

Diffusion in earth systems frequently occurs through complex, heterogeneous media, where more than one phase or pathway exists and each phase has its own distinct chemical and physical properties (Fig. 2; Text Box 4). Complexities could include multiple phases characterized by distinct diffusivities, differences in diffusive length scales (grain sizes), variations in interconnectivity of fast pathways (e.g., fluids), and differences in the concentration of the diffusant within each phase or pathway. Diffusive mass transfer within such poly-phase and/or heterogeneous systems is commonly referred to as bulk diffusion (Text Box 4). In its simplest conceptualization, the bulk diffusivity, \( D_{\text{bulk}} \), is a continuum property of a heterogeneous material that captures its overall diffusion behavior, and at sufficiently large length scale – much larger than any individual heterogeneities – \( D_{\text{bulk}} \) can be invoked using the equations in Section 2. However, the concepts and formalisms of bulk diffusion can be applied at a number of scales (Fig. 2), including individual mineral grains (lattice+ defects) as well as rocks (minerals+ITM).

A familiar example of bulk diffusion is diffusive mass transfer through a porous medium (e.g., fluid saturated soil, sediment or rock), such as mineral grains permeated by an intergranular fluid medium. Diffusion in the fluid is much faster than in the solid grains, so long-distance diffusive transport is mediated entirely by the fluid (this is analogous to type c grain boundary diffusion in the classification of Harrison [30]). Baxter and DePaolo [31] used the term intergranular transporting medium (ITM; conceptually similar to Brady’s [32] IGR) in reference to this high-diffusivity medium. The properties of the ITM represent the bulk continuum properties of the intergranular region, which in actuality may comprise grain boundaries alone or a combination of one or more C–O–H fluids and/or melt in addition to partially wetted grain boundaries (see Fig. 2). If the solid phases are assumed to be free of (and inert to) the diffusant of interest (e.g., hydrocarbons diffusing through a pure quartz sandstone) then an “effective diffusivity” may be defined:

\[
D_{\text{eff}} = bD_{\text{ITM}}\phi
\]

where \( \phi \) is the porosity (volume fraction of ITM) and \( b \) is the tortuosity of the interconnected fluid pathway.

In many earth systems, the solid grains themselves hold much of the diffusant and at high temperatures may influence the bulk diffusive behavior of the system (e.g., Sr diffusion through a partially molten rock). Here, the bulk diffusivity becomes a strong function of the partitioning of the diffusant between the ITM (where long-range transport occurs) and the solid (where some or most of the diffusant is stored). Assuming, for the moment, that the solid grains maintain local equilibrium with the ITM (with respect to the diffusant), then at any location in the system, the ratio between the diffusant concentration in the bulk solid and the ITM is, by definition, the solid/ITM partition coefficient, denoted here as \( K_{\text{ITM}}^{\text{solid}} = C_{\text{solid}}/C_{\text{ITM}} \). The effective bulk diffusivity is obtained by modifying Eq. (5) to account for the fraction of the diffusant held in the solids:

\[
D_{\text{bulk}}^* = \frac{\rho_{\text{ITM}} bD_{\text{ITM}} \phi}{\rho_{\text{solid}} (1-\phi) K_{\text{ITM}}^{\text{solid}}} = \frac{bD_{\text{ITM}}}{MK_{\text{ITM}}^{\text{solid}}}
\]

where \( \rho \) is the density and \( M \) is the mass ratio of solid to ITM in the system. We can express a characteristic bulk diffusive timescale, \( \tau_{\text{bulk}} \), by introducing a relevant length scale, \( L \), for the system as follows:

\[
\tau_{\text{bulk}} = \frac{L^2}{D_{\text{bulk}}^*}
\]
This bulk diffusive timescale describes the ease with which a particular diffusant is transported in a given bulk system, including the contributions of all solid and ITM phases. This parameter may more generally be called a “transmissive timescale” [33] because other transport processes (e.g., advection) might exist. The importance of the porosity, \( \phi \), of the system has long been appreciated by researchers studying chemical transport in porous media. More recent study has focused on the equal importance of \( K \) in controlling bulk diffusion. Transport through the ITM, however rapid, is only efficient if a significant amount of the diffusant is in the ITM. This can be quantified using the mineral/ITM partition coefficient, \( K \), but data are scarce; acquisition of mineral/ITM partitioning data is a research frontier in itself.

The bulk diffusivity, \( D_{\text{bulk}}^\ast \), defined above is applicable whenever it can be assumed that the solid and ITM can maintain equilibrium with each other over the time and length scale of interest. When this assumption breaks down, bulk diffusion in heterogeneous media becomes more complicated, but is still amenable to modeling. This equilibrium assumption is evaluated by comparing the characteristic timescales for diffusive transport within the ITM (\( \tau_{\text{ITM}} \)) and the “equilibration” timescale of the solids with the ITM (\( \tau_e \)),

\[
De = \frac{\tau_{\text{bulk}}}{\tau_e}
\]

where \( De \) is a “diffusive-exchange parameter”. Equilibration of the solid with the ITM may proceed by a net transfer process such as dissolution-precipitation [31,34,35], grain boundary migration [36,37] or by solid-state diffusion [38,39]. When equilibration is controlled by solid-state diffusion, such systems have been called “double-diffusive” and represent one important subset of “multi-diffusion” systems (Text Box 4). An example of a double diffusive system with application to excess Ar in thermochronology is provided in Section 3.3.5.

3.3. The diffusive closure concept and thermochemistry

3.3.1. The Dodson equation

Because so many interpretive geochemical applications (e.g. geo- and thermochemistry, geothermobarometry) rely on the assumption or knowledge of equilibration between phases, it is fundamental to rigorously predict the last time and conditions after which diffusive re-equilibration between phases is no longer significant and geochemical/geochronological information is locked in. This non-instantaneous transition between open (equilibrating) and closed (locked in) behavior is called “closure”. Jaeger [40] suggested long ago that different minerals close to diffusive loss of certain radiogenic daughter elements (such as Ar, Sr, Pb, He) at different temperatures (their “closure temperatures”)—an observation soon understood in the context of the temperature-dependent character of diffusion (Eq. (3)). Dodson [41] formalized the concept of mineral closure and derived what is now known as the “Dodson Equation”, which includes the important effects of Arrhenius diffusion parameters (the constants in Eq. (3)) for the element in the mineral of interest, the characteristic diffusion length scale and geometry, and the cooling rate (Dodson used monotonic cooling, \( T \propto t^{-1} \), in his derivation). The Dodson equation has proven valuable in illuminating many of the key factors that determine a mineral’s closure temperature, but several of the assumptions of the Dodson formulation must be carefully assessed in any given situation. Limitations of the Dodson Equation have been discussed at length elsewhere [42,43]; Cherniak and Watson [44] discuss diffusive closure in the context of thermal events other than monotonic cooling, showing (among other things) that simple heating of an initially cool mineral to its ‘closure’ temperature for a particular diffusant will result in 40% loss of that diffusant (this statement holds for any heating rate as long as it is equivalent to that used to calculate the closure temperature). Here we focus mainly on issues arising from the gradual nature of closure and the complexities of natural systems.

3.3.2. The partial retention zone

The assumption of monotonic cooling from an arbitrarily high temperature does not apply to every system. Many minerals dwell for extended periods in a “partial retention zone” between complete diffusive openness and complete diffusive closure. Ganguly and Tirone [45] have dealt with this problem for high temperature thermochronometers and thermometers, and much of modern low-temperature thermochemistry involves quantification and modeling of these effects, for example in He-thermochronology [46]. While more cumbersome and sometimes non-unique, rigorous numerical approaches are easily applied to even the most complex thermal histories.

3.3.3. Characteristic length scale and diffusivity for mineral closure

Dodson assumed that the macroscopic mineral grain radius and the lattice diffusivity determine the characteristic timescale for diffusive loss. The sub-microscopic complexities of natural minerals (Fig. 2) raise doubt
about the validity of these assumptions, especially for noble gases. It is now clear, for example, that the macroscopic grain size has virtually no bearing on the diffusive loss characteristics of Ar from K feldspar [47]. Rather, multiple intracrystalline domains of varying size control Ar diffusive loss. Individual domains conform to the Dodson formulation, and thus each domain carries with it information about a different temperature on a T–t path. While questions persist about the physical basis for the MDD concept, recent work [48] has begun to illuminate the intragrain properties that lead to MDD behavior in feldspars. Ongoing research suggests that multi-path diffusion may characterize other minerals such as titanite and quartz [49,50], fundamentally changing the way diffusive loss (or uptake) should be modeled.

3.3.4. Boundary conditions for mineral closure

Dodson’s formulation carries an important yet too-often overlooked assumption—namely that the surroundings of the mineral of interest behave as an effectively infinite sink for the escaping diffusant. Common practice is thus to ignore the surroundings of the mineral of interest in applying the closure concept—indeed, there are no parameters describing the rest of the rock system within Dodson’s equation. But as different minerals close at different times and temperatures and as the capacity for the ITM to accept and transport a diffusant varies, this assumption may break down. Stated differently, even if a mineral remains diffusively open (according to Dodson’s equation), if it has nothing to exchange chemistry with, it will be effectively closed. Eiler et al. [51] and Jenkin et al. [52] have discussed this issue as it applies to oxygen isotope thermometry and Rb–Sr geochronology, respectively, by assuming rapid diffusion within the ITM and modeling the progressive closure of all local mineral phases. The situation for noble-gas based geochronometers is slightly different, as discussed below.

3.3.5. Case study: the importance of bulk diffusion in thermochronology

In the case of noble-gas based thermochronometers (K–Ar and U/Th–He), the infinite sink assumption of Dodson’s equation implies that the concentration of the escaping noble gas at the mineral surface is always effectively zero. If true, this zero-concentration boundary condition prevents Ar (or He) accumulation in the mineral of interest before its closure interval, conveniently linking the closure temperature with the measured radiogenic age—the basis of thermochronology. While this assumption seems to be valid in many cases, and may almost always be true for helium [53], the ubiquitous occurrence of “excess Argon” shows that it does not always hold [54,55]. Baxter [33] showed that the zero-concentration boundary condition can be met in one of two ways: 1) if the Ar (or He) released into the surroundings can be transported away from the system significantly faster than it is produced, and/or 2) if the partitioning of Ar (or He) between the mineral of interest and its surroundings strongly favors the surroundings. Here, the importance of partitioning between minerals, fluids and melts [55], and dry grain boundaries [56] is illuminated. These effects are encapsulated in a single equation showing how excess Ar (expressed as an age-equivalent) builds up in a mineral prior to its closure. Two factors are important: 1) the “transmissive timescale”, \( \tau_T \), for transport of Ar out of the system to an effective sink a distance \( L \) away, and 2) the “total local sink capacity” (TLSC) of the surroundings relative to the mineral of interest.

Fig. 5. Arrhenius diagram illustrating the nature of the extrapolation often required to apply laboratory diffusion data to crustal geologic systems. The temperature scale is arbitrary because no particular diffusion law is assumed, but the diffusivity scale has meaning in terms of what can be measured in the laboratory. The minimum measurable value is determined by the available time (realistically, a few months) and the spatial resolution of the analytical technique. Rutherford backscattering spectroscopy (RBS) and secondary-ion mass spectrometry (SIMS) have the best resolution available in depth-profiling mode. The minimum diffusivity measurable using RBS (depth resolution \( \sim 10 \) nm) is \( \sim 10^{-23} \) m\(^2\)/s. This value is high enough to result in appreciable diffusion over the vast time scales of some natural diffusion phenomena (10 s of microns in 1 Myr, \( \sim 1 \) cm in 1 Gyr).
including equilibrium partitioning and modal abundance effects:

\[
^40Ar_{\text{age-equivalent}}(L, t) = \frac{\tau_T t}{2} \left(1 - \exp\left(-\frac{5/2}{\tau_T(1 + TLSC)} t\right)\right)
\]

(note the minus sign preceding the 5/2 constant is a correction from Baxter [33]). Here, \(\tau_T\) is defined as the bulk diffusive timescale for Ar (or He) as in Eq. (7). This equation is valid for Ar bulk diffusion through the ITM with the required assumption that all minerals in the system (Ar sources and sinks) are open and able to maintain equilibrium with each other and with the ITM. In practice, noble gas thermochronology is most rigorously modeled as a double-diffusive system (cf. Text Box 4) including the diffusion of Ar within the mineral of interest and the surrounding sink minerals, as well as bulk diffusion of Ar out of the system through the ITM. When any minerals in the system begin to pass through their respective closure intervals, the above equation breaks down because the system must be treated as double-diffusive, and further calculations must be performed numerically. This is an example of the applicability and importance of bulk and double-diffusive regimes in geochronology.

3.4. ‘Natural’ vs. ‘laboratory’ diffusion

There is a marked contrast between the time scales available in the laboratory to study diffusion and the time scales relevant to natural transport processes. This unavoidable fact necessitates care and wisdom in the comparison (and reconciliation) of observations from the two realms (e.g., [43]). Experimentalists who characterize diffusion in the laboratory cling to the theoretical principle that lattice diffusivities are true constants that apply for all time under appropriate and comparable conditions. Although generally defensible, this viewpoint does not circumvent the unavoidable reality that laboratory determinations of \(D\) are commonly made at temperatures significantly higher (and timescales much shorter) than those of interest in nature, particularly when the experiments target a crustal phenomenon. Down-temperature extrapolation of measured diffusivities to geologically realistic temperatures is often necessary (see Fig. 5). The principal risk in this approach is that low-temperature diffusion behavior may be dominated by a different pathway, in which case the high-temperature data paint an inaccurate picture. Wartho et al. [57] showed, for example, an apparent change in Arrhenius laws for Ar diffusion in K feldspar below about 725 °C. The prevalence of such behavior is unknown, but frequent agreement between high-temperature data and natural constraints on diffusion (see below) suggests that the problem is not pervasive. Lattice diffusivities measured in the laboratory should not be assumed, indiscriminately, to apply to all natural cases, but this does not lessen the value of the measurements: at some length (and time) scale, it is lattice diffusion specifically that governs diffusive
exchange between a mineral and its surroundings. Because of the high temperatures prevailing in the mantle relative to the crust, experiments can often be conducted at the temperatures of direct interest, so down-temperature extrapolations are not always necessary.

The diffusivities governing in situ diffusion in natural systems can sometimes be estimated directly from measurements on rocks and minerals. Diffusion behavior can be deduced from isotopic closure systematics and from observed chemical gradients coupled with independent constraints on thermal history. Additional insights into diffusion in natural samples can be gained from the diffusive loss characteristics of Ar and He in the extraction line of a mass spectrometer. ‘Real-world’ characterizations of diffusion are often in good agreement with laboratory measurements; examples include: Pb diffusion in zircon (e.g., [58,59]), monazite (e.g., [63,64]) and apatite [65,66]. Carlson [67] noted generally good agreement between laboratory and natural constraints on divalent cation diffusion in garnet.

The most common cause of discrepancies between lab and nature may be ‘imperfect’ growth conditions of natural crystals or a history of deformation and recrystallization, either of which could result in fast paths [68,69]. Fig. 6 depicts two forms of direct evidence that fast-path contributions will complicate the diffusion behavior of what are apparently single crystals. The abundant evidence for multi-path diffusion of noble gases also underscores this point, although it is not yet known whether other diffusants are subject to similar effects. Other factors besides the mere existence of high diffusivity pathways are important in this context, most notably the partitioning of the diffusant between the fast path and the lattice (see 3.2).

In summary, the advantage of laboratory-determined diffusivities is that we can usually be fairly certain what has been characterized; the disadvantage is that downward extrapolations in temperature are often required to apply the data to natural systems, and if natural samples are dominated by fast-paths not present in the lab sample, the laboratory value represents only part of the information needed. The strength of diffusion information obtained from natural rocks is that it can be applied with confidence to the specific material that was characterized; the drawback is the uncertainty about the transport path and the soundness of generalizing to other samples and conditions. Continued effort to ‘reconcile’ laboratory with nature are an important frontier in diffusion studies; for the most part, this means discovering the full range of factors that contribute to multi-path diffusion and the circumstances under which these come into play.

3.5. Effect of H₂O and H species on diffusion

Dissolved H₂O in magmas has a pronounced enhancing effect on diffusion of most constituents [70], which is reasonable given the de-polymerization of the melt that accompanies H₂O dissolution (e.g., [71]). The effect of H species on diffusion in crystals is less well understood, but it stands to reason that intracrystalline diffusion can be affected only if H species enter the lattice. It has been recognized for some time that the presence of H₂O in the system of interest can dramatically affect lattice diffusion of oxygen in the crystalline phases present, including quartz [72–75], calcite [76,77], alkali feldspar [75,78], clinopyroxene [79], zircon [80], monazite [81], rutile [82], olivine [83,84] and sphene [49].

The effect is almost always an enhancement of oxygen diffusion by the presence of H₂O, but in rutile the relationship is more complex [82]. In some cases, $D_{lattice}^{oxygen}$ shows a systematic increase with increasing $P_{H_2O}$ [74,79], but in other instances the relationship between $D_{lattice}^{oxygen}$ and H₂O appears to be ‘binary’: i.e., fast diffusion is ‘turned on’ at some low threshold value of $P_{H_2O}$ but changes relatively little over large subsequent increases in $P_{H_2O}$ [80]. The generally accepted explanation for H₂O-enhanced oxygen diffusion is that neutral water molecules are somewhat soluble and highly mobile in the crystal lattice [85,86]. These mobile H₂O molecules serve as ‘long-distance carriers’ of oxygen, and exchange oxygen with the lattice locally.

Given the probable mechanism of oxygen diffusion enhancement by H₂O, it is perhaps not surprising that lattice diffusion of cations appears generally insensitive to changes in $P_{H_2O}$, with certain important exceptions. Existing experimental studies suggest a limited role for H in lattice diffusion of cations at crustal P–T conditions. Kronenberg et al. [87], for example, concluded that the presence of H₂O does not affect C diffusion in calcite. Cherniak and Watson [58] showed that $D_{Pb}$ in zircon in the presence of hydroxyapatite (but no fluid phase) is indistinguishable from $D_{Pb}$ in zircon under H-absent conditions. Perhaps more convincing is the fact that independent characterizations of Sr diffusion under dry and H₂O-present conditions for both feldspar and apatite are in substantial agreement [88–90,65], and there are numerous examples of agreement between inferred isotopic closure behavior in natural systems (reasonably inferred to contain some H species) with laboratory characterizations of diffusion under dry conditions (see Section 3.4). Watson and Cherniak [91] examined Ar diffusion in quartz under nominally dry and H₂O-present conditions and did not find a significant difference. Cherniak and Watson [44] showed that Ti diffusion in...
zircon is unaffected by a change from dry conditions at atmospheric pressure to $P_{H_2O}=0.6$ GPa.

The effect of H$_2$O on lattice diffusion of cations in deep-seated mantle phases is a quite different story, perhaps because the available lattice solution mechanisms for H-bearing species are different. Recent studies have revealed significant enhancement by H$_2$O of Si self-diffusion [84] and Fe–Mg interdiffusion in olivine [92, 93]. These effects are probably responsible for enhancement of kinetic properties such as viscosity, grain-growth rate and phase transformation kinetics [94–98]. In the Fe–Mg case, diffusion enhancement has been traced to the entry of H$^+$ into the lattice and consequent changes in point-defect concentrations (cation vacancies). The enhancement of $D_{Fe–Mg}$ is roughly proportional to the increase in water fugacity, leading to a $\sim 50$-fold increase in ‘wet’ Fe–Mg interdiffusion over the dry case at 5 GPa and 1100 °C. A similar but smaller effect has been observed for Fe–Mg interdiffusion in ferro-periclase [99].

3.6. Diffusive fractionation of isotopes

The phenomenon of (isotopic) mass-dependent diffusion in gases has been recognized for decades, and formed the basis of early efforts to separate isotopes. Until recently, the effect has been considered only sporadically for geologically relevant diffusants and condensed phases. In olivine and clinopyroxene, Trull and Kurz [102] observed a significant difference in the diffusivities of $^3$He and $^4$He (for which the mass effect might be relatively large), and Tsuchiyama et al. [103] made theoretical predictions about isotopic effects on diffusion of heavier elements in molten MgO. Trull and Kurz [104] later noted differences in He isotope diffusivities of several percent in basaltic glass. Also in 1999, Richter et al. [105] demonstrated experimentally for the first time that isotopes of a relatively heavy element ($^{40}$Ca and $^{44}$Ca) have slightly different diffusivities in CaO–Al$_2$O$_3$–SiO$_2$ melts. This mass effect on diffusion was later extended by Richter et al. [106] to melts of basaltic and rhyolitic composition. It was also confirmed for Li isotopes ($^6$Li and $^7$Li), where a substantially larger effect was observed. Richter et al. [105] adopted the mathematical form of the mass dependence expected from the kinetic theory of gases

$$\frac{D_1}{D_2} = \left(\frac{M_2}{M_1}\right)^\beta \quad (10)$$

where the $D$ ratio is the diffusivity of isotope 1 over that of isotope 2, and $M$ refers to isotope mass. For gases, the exponent $\beta$ is 0.5, but the results for Li and Ca isotopes in silicate melts reveal smaller $\beta$ values of 0.215 and 0.075, respectively. These $\beta$ values lead to small absolute differences in $D$ for two isotopes (the difference appears in the second or third decimal place), but these differences can produce rather large isotope fractionations under the “right” circumstances. As discussed by Richter et al. [106], the potential for diffusive fractionation is maximized when two interdiffusing reservoirs have markedly different concentrations of the element whose isotopes are under consideration. The most extreme case is when one of the reservoirs is essentially devoid of the element of interest, as
illustrated in Fig. 7. These dramatic diffusive fractionations require special circumstances in order to develop in natural systems, but plausible scenarios do exist. Fractionation effects due to diffusion in melts might be expected in the margins of mafic magma bodies emplaced in the continental crust, in vapor bubbles exsolving from a magma, and in magmatic double-diffusive situations.

Richter et al. [107] extended their studies of diffusive isotopic fractionation to aqueous solutions at near-ambient conditions, where substantial smaller effects are observed ($\beta$ in Eq. (10) is $\sim 0.01$–$0.03$). The documentation of mass-dependent diffusivities in silicate melts at high temperatures and in aqueous solutions at low temperatures raises the likelihood that geologic media ‘intermediate’ between these two — e.g., supercritical fluids laden with silicate solute — might exhibit the same effect. This has not yet been demonstrated experimentally, but the recent study by Teng et al. [108] of amphibolite country rock against an alkalic pegmatite strongly suggests fractionation of Li isotopes by diffusion in either a fluid phase or in the grain boundaries of the amphibolite ($^{7}$Li/$^{6}$Li fractionation $>20\%$ was observed). Whichever diffusion medium is responsible, similar effects might be envisioned for the interaction between down-going slab and overlying mantle wedge in subduction zones.

The documentation of mass-dependent diffusion in a variety of geologic media (gases, aqueous solutions, and molten silicates) begs the question as to whether it also occurs in minerals for elements other than light noble gases. Studies of metals (e.g., [109]) suggest that the answer is yes, but direct measurements on minerals will be difficult because diffusion distances achievable in the lab are generally small and depth-profiling analytical techniques may therefore be required. The mass effect appears largest in gases at low pressures, markedly smaller in dense (silicate) liquids, and still smaller in aqueous solutions. On the basis of observed behavior in gases and silicate melts, we speculate that the mass effect will be quite small in dense crystalline oxides, where the kinetic energy of the atoms is almost entirely vibrational (see Section 2.2).

In closing this section, we note that, unlike equilibrium fractionation, diffusive fractionation does not go away at high temperature — it can occur at all temperatures where diffusion is effective [106]. This does not mean that we should expect ubiquitous occurrences, however, because diffusive fractionation will be apparent only in a system that fails to reach equilibrium: it is a consequence of an interrupted process. Lastly, the magnitude of an observed mass effect on diffusion of a particular element will depend strongly upon the identity of the diffusing species. Aqueous solute ions, for example, carry large spheres of hydration, and it is the mass (and size) of the entire complex that will determine the value of $D$. Differences arising from the identity of the solute isotope of interest will be minimized in this case [107]. The same effect could operate in magmas, where elements of potential interest dissolve (and may diffuse) as molecules or complex anions (e.g., CO$_3^2$ or CO$_2$ in the case of carbon [110]).

3.7. Diffusion in the deep Earth

Studies of diffusion have been conducted on Earth materials for several decades, but it is only recently that the experimental technologies (and computational approaches (e.g. [111])) have been available to explore diffusion in the deep Earth — i.e., at $P > 3$ or 4 GPa (see [25] and references therein). Given the form of Eqs. (3) and (4) and knowledge of the deep geothermal gradient, the key question is how the enhancing effect of increased $T$ on diffusion plays off against the suppressing effect of increased pressure. In this regard, it is important to bear in mind (given the form of Eq. (3)) that a temperature increment of, say, 100$^\circ$ has a progressively smaller effect as temperature rises along the geothermal gradient. The interplay of the effects of temperature and pressure along the geotherm is illustrated in Fig. 8 for a hypothetical phase that is stable over the entire range of $P$–$T$ conditions in the mantle. No such phase exists, but the plot is nevertheless useful in revealing the dominance of the temperature.

![Fig. 8. Diffusivity along the mantle geotherm in a hypothetical phase that is stable over the entire pressure range. Typical diffusion parameters were assumed as follows (see Eqs. (3) and (4)): $D_x = 1 \times 10^{-6}$ m$^2$ s$^{-1}$; $E_a = 300$ kJ mol$^{-1}$; $V^* = 3$ cm$^3$ mol$^{-1}$. The geotherm (inset) is an average based mainly on the information in Duffy and Hemley [165], and is given for $P = 1$–15 GPa by $T(K) = 1900$–1420 · $0.8^p$ and for $P = 16$–140 GPa by $T(K) = 1680 + 11.1 \cdot P$.](image-url)
effect at shallow depth and the counteracting effect of pressure deep in the Earth. The diffusivity along the entire lower-mantle geotherm changes by only about 2 orders of magnitude despite a temperature difference of \(~1400\)°. Real-world phase transitions would obviously affect this oversimplified picture [26,112].

Revisiting the approach of Hofmann and Hart [113], Holzapfel et al. [28] applied their new data for Fe–Mg interdiffusion in the perovskite lattice to evaluate diffusive equilibration time scales in the lower mantle, concluding that the length scale of diffusion over the entire age of the Earth is only about 1 m. This result contrasts with that of Van Orman et al. [114] for cation and oxygen diffusion in MgO at pressures up to 25 GPa. Lattice diffusion in this phase is fast enough to lead to diffusive length scales of 1–10 km over the age of the Earth (100 km if grain boundary transport controls the diffusive flux). Given a perovskite-dominated lower mantle, the question of whether subordinate magnesiowüstite grains are interconnected becomes of paramount importance (isolated grains of a high-diffusivity phase would have little effect on bulk transport).

One of the key questions concerning deep-Earth diffusion is to what extent the metallic core communicates with the silicate mantle, and what elements are involved. This topic was addressed in early studies by Knittle and Jeanloz [115] and Goarant et al. [116] focusing specifically upon the rate of reaction between metal and oxides. A broader attack on this general problem will undoubtedly occur over the coming decade, given the ongoing debate about possible core–mantle ‘communication’ with respect to certain siderophile elements [117–121]. Some siderophile elements have been shown to be extremely mobile in MgO grain boundaries at modest pressures [122,123].

3.8. Bulk diffusion of molecular H₂O

Water, and its transport within the Earth, is central to many important geochemical questions which go far beyond the scope of this paper. Consider, for example, the global water cycle represented by the hydration of the oceanic lithosphere, the subduction and de-watering of the slab, the release of H₂O into the fore-arc and mantle wedge, and the fluxing of arc magmatism. The processes within this cycle are topics of concentrated research in the geoscience community, and yet the mechanisms and rates by which H₂O is transported and exchanged within these systems are not well constrained. Certainly, advection of aqueous fluids (or supercritical fluids) operates in many systems [124–126], but if that flow is channelized, then at some local length scale, diffusive transport of water to and from such channels (e.g.,[127,128]) is rate limiting in the net hydration or dehydration of a rock system.

On the input side of the subduction zone, Ranero et al. [129] suggest that hydration of the oceanic crust and mantle is promoted by channelized flow down flexure cracks. However, the overall effectiveness of hydration depends upon the extent of H₂O migration from the cracks into the adjacent rock. This would occur via either grain-boundary diffusion of H₂O molecules or penetration of fluid along grain edges by dissolution/ precipitation processes [130], or both. The latter process is controlled by solute diffusion through interconnected fluid, but can occur only if grain-edge wetting is energetically favorable [130]. In either case, the bulk diffusive length scale, L, would be represented by the half width between flexure cracks. Experimental constraints and modeling of the bulk diffusion of H₂O coupled with hydration and dehydration reaction kinetics within subduction zones is another important frontier.

3.9. Geospeedometry: constraining the durations of geologic processes

Geospeedometry [131] refers to the use of diffusion profiles within minerals to extract information about the timescale of a particular geologic process. Whereas geochronology is generally geared toward the specific age of an event, geospeedometry is theoretically capable of providing unique information about the duration or episodicity of that event. Further interpretations may in some cases permit evaluation of the rate of a particular process — i.e., the ‘speed’ in geospeedometry. Conceptually, if the Arrhenius law of a particular species in a mineral is well known, and if an ‘unfinished’ diffusion profile is captured in a mineral, then the duration over which diffusion occurred can be determined. Geospeedometry is thus capable of elucidating very short-lived events that traditional geochronology cannot resolve. Recent years have seen a resurgence of this methodology, in particular as chemical diffusion data have continued to improve. Examples include the use of chemical profiles in igneous phenocrysts to constrain eruptive timescales and cooling rates (e.g. [132–135]) and chemical profiles in metamorphic minerals to constrain the duration of metamorphism and related processes (e.g., [136–138]). Watson and Harrison [139] described a method to extract \(T–t\) information from stranded profiles of two diffusants governed by independent Arrhenius laws. As additional high-quality experimental data on diffusion become available, this
and other approaches in geospeedometry may reach their full potential.

3.10. Computational sources of data

This discussion would not be complete without brief mention of theoretical means to obtain diffusion ‘data’ for use in modeling geochemical systems, as this is an important frontier in itself. Oelkers and Helgeson [140] were early contributors in this area who constrained diffusion of a variety of ions in supercritical aqueous fluids using available electrical conductance measurements and the Nernst–Einstein equation. Recently, theorists have turned to computational approaches to generate diffusion ‘data’ for both solids and liquids. Molecular dynamics simulations—which explore large ensembles of atoms using interatomic potentials to calculate equilibrium and transport properties—are particularly promising (e.g., [103,141–154]). These approaches have not yet eliminated the need for constraints from the experimental lab and natural systems, but we can expect computational modeling and direct measurements to go increasingly hand in hand in future studies.

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